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Study of crystallization processes in some rare earth vanadate, tungstate and phosphate systems under hydrothermal conditions

K Byrappa and B Nirmala

Department of Geology, Mysore University, Manasagangotri, Mysore-570 006, India

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Abstract : The study of physico-chemical hydrothermal reactions has been carried out for the growth of some selected rare earth vanadate, alkali rare earth tungstate and phosphate crystals. The possible crystallization processes have been formulated, which help in the sharp reduction of the PT conditions of the growth of these crystals under hydrothermal conditions

Keywords : Hydrothermal growth, rare earth vanadates, alkali rare earth tungstates, phosphates crystallization processes

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1. Introduction

Hydrothermal synthesis is the use of aqueous solvents or mineralizers under the action of temperature and pressure to dissolve and recrystallise materials that are relatively insoluble under ordinary conditions [1]. Although the hydrothermal research began during 1840s, till 1970s, the interest was mainly geological in order to simulate the natural conditions of high pressure and temperature in the laboratory. However, the intense studies began in 1960s and 1970s, and the interest was confined to the creation of mainly higher PT conditions, PVT relations, particularly in the aqueous media and crystal growth. Until recently, there was no work on the physico-chemical and hydrodynamic principles of the hydrothermal growth of crystals. Even the solubility data was not available for many compounds and the method appeared quite complicated. The greatest disadvantage of this technique is the "black box" like nature of the autoclaves, and their maintenance. Thus during late 1970s and 1980s the interest in hydrothermal technique declined considerably, and at the same time, there was an entry of physical chemists, organic chemists and so on.

2. Hydrothermal physical chemistry

This is perhaps the least known aspect in the hydrothermal growth of crystals. The basic properties of the hydrothermal medium like viscosity, dielectric constant, compressibility and coefficient of expansion are to be understood in the crystal growth context. Since diffusion is inversely proportional to the solvent viscosity, one can expect very rapid diffusion in hydrothermal growth. Here, it is appropriate to acknowledge the works related to the behavior of the solution at lower PT conditions by Franck [2], Seeward [3] and Hegleson [4]. Though most of these studies do not give an insight into the complete physical chemistry of the hydrothermal media as they represent mainly the lower PT conditions, a trend was set in this direction.

The composition and concentration of the solution, temperature, pressure and hydrodynamic conditions, are some of the basic physical and chemical parameters, which determine the regime and rate of dissolution of the nutrient, mass transport and possibility of the formation of phases.

There are several processes, which commonly occur during hydrothermal reactions like hydrolysis, polymerization, complexation, solvent-solute interaction, formation of polymeric and anionic species.

In recent years there has been some good progress achieved on the experimental side. The author [5–7] has studied the physical chemistry of the hydrothermal growth of malachite, A_2B_6 and tellurium dioxide crystals. Similarly there are several works on the hydrothermal crystallization kinetics, intelligence engineering of the hydrothermal reactions and so on [8–10]. More recent developments in the field of hydrothermal physical chemistry and hydrodynamic principles have been discussed in [1]. Such studies have rekindled interest in hydrothermal technique, and also solved many of the existing basic problems in the hydrothermal growth of crystals.

With regard to the hydrothermal solution chemistry, it is important to understand the properties of water like its viscosity, density, and conductance as a function of temperature and pressure [2–4,11]. It has been demonstrated for many cases that the mineralizer solutions are closer to the properties of water. Franck [2] has discussed the conductance of hydrothermal solutions, which remains high in spite of decrease in ϵ, because that effect is more than compensated by an increase in the ion mobility brought about by decreased viscosity under hydrothermal conditions. As the dielectric constant of water decreases with increasing temperature at constant pressure and/or decreasing pressure at constant temperature "completely" dissociated electrolytes at low temperatures, and pressures may become highly associated in the supercritical region [12]. A complete PVT data for water and other solvents are rather rare. However, PVT data for water is known up to 1000°C and 10 Kb accurately [13,14]. At very high pressure and temperature conditions (1000°C and 100 Kb) water is completely dissociated into H_3O^+ and OH^- behaving like a molten salt and has a higher density of 1.7–1.9 g/cm^3 [15]. The high mobilities of H^+ and OH^- ions are expected in water solutions. When concentrated solutions are used, the critical temperature

can be several hundred degrees above that of pure water [16]. Therefore, the structure of the supersaturated solutions under hydrothermal conditions has to be understood precisely, because it can give information on the thermodynamics of stability of the solutions, nucleation and its relation to cluster evolution, and metastable solutions and their properties. There are various means of studying these aspects like pH measurements, calorimetric studies and the Raman Spectroscopy. The present authors have investigated some of these aspects based on the pH and calorimetric data for some selected vanadate, tungstate and phosphate systems.

3. Hydrothermal crystal growth

Crystal growth processes under hydrothermal conditions can not be observed directly. In fact, no theoretical basis for the hydrothermal processes has been fully established. The present authors have attempted to study the crystal growth processes involved in the growth of some selected rare earth vanadates, tungstates and phosphates compounds under hydrothermal conditions.

Many inorganic ions, including $(OH)^-$, Cl^-, F^-, S^{2-}, NH_4^+, H^+ and WO_4^{2-}, act as effective mineralizers. The complexates formed by these mineralizers should not be stable, such that they themselves precipitate [17].

A full understanding of the complex system formed in solution is inconceivable without studying the physical and chemical effects of the solvent on the dissolved ionic species [18]. These properties are involved in such a complex interaction that it is difficult to establish unambiguously how they contribute individually to the general behaviour of the solvents and its interaction with the solute.

3.1. Hydrothermal growth of rare earth vanadates :

Single crystals of rare earth vanadates, RVO_4 with zircon structure $ZrSiO_4$ having tetragonal space group I_4/amd [19] find extensive applications owing to their valuable unusual magnetic, optical and luminescent properties. There are many reports on the growth of rare earth vanadates using flux and melt techniques. However, there are no reports on the growth of RVO_4 by hydrothermal method.

The authors have succeeded in growing the RVO_4 at low temperature and pressure under hydrothermal conditions [20,21]. The starting materials such as R_2O_3 (R = Y, Gd), V_2O_5, Nd_2O_3 in desired molar ratio and calculated amount of HCl + HNO_3 were taken in a teflon liner. The experiments were carried out in Morey autoclaves provided with teflon liners at 240°C and pressure 80–100 bars. Crystallization was carried out in all the experiments through spontaneous nucleation. The following reaction series can be proposed for the formation of RVO_4 :

$$V_2O_5 + 10HCl \rightarrow 2VCl_4 + 5H_2O + Cl_2 \uparrow \quad (1)$$

$$R_2O_3 + 3HCl \rightarrow R(OH)_3 + RCl_3 \quad (2)$$

$$R_2O_3 + 6HNO_3 \rightarrow 2R(NO_3)_3 + 3H_2O \quad (3)$$

$$V_2O_5 + 6HNO_3 \rightarrow 2H_3VO_4 + 3N_2O_5 \uparrow \quad (4)$$

$$2VCl_4 + 4HNO_3 \quad 2VOCl_3 + 2HCl + H_2 \uparrow + 2N_2O_5 \uparrow \quad (5)$$

$$2VOCl_3 + 8R(OH)_3 \quad R_8V_2O_{17} + 6HCl + 9H_2O \quad (6)$$

$$2VOCl_3 + 2R(NO_3)_3 \quad 2RVO_3 + 3N_2O_5 + 3Cl_2 \uparrow \quad (7)$$

$$RCl_3 + H_3VO_4 \quad RVO_4 + 3HCl \quad (8)$$

$$VOCl_3 + R(OH)_3 \quad RVO_4 + 3HCl \quad (9)$$

$$2H_3VO_4 + 2R(NO_3)_3 \quad 2RVO_4 + 3H_2O + 3N_2O_5 \uparrow \quad (10)$$

$$H_3VO_4 + R(NO_3)_3 \quad RVO_4 + 3HNO_3 \quad (11)$$

$$H_3VO_4 + R(OH)_3 \quad RVO_4 + 3H_2O \quad (12)$$

The crystals obtained by this method were of good quality, generally show dark brown to light brown colour with a change in the dopant level. The growth rate and morphology of the crystals depend mainly on the pH of the growth media, temperature and pressure (percent fill). A study of the growth rate of the rare earth vanadate crystals was attempted. Figures 1 and 2 show morphology variations with pH and pressure (percent fill)

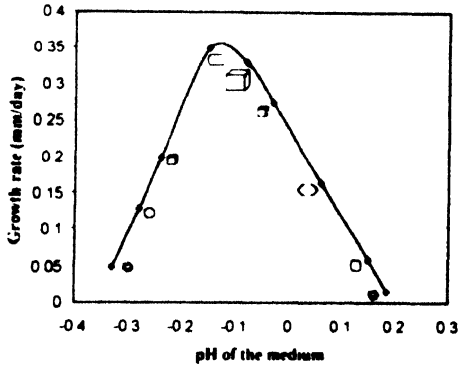

Figure 1. Dependence of growth rate and pH of the growth media of Nd YVO_4

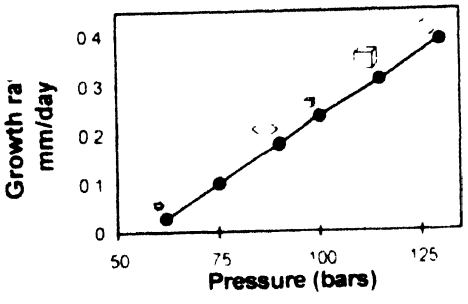

Figure 2. Morphology variation with pressure of Nd YVO_4

The authors have studied the solubility of rare earth vanadates within a wide range of PT conditions. RVO_4 (R = Y, Gd) shows a negative temperature coefficient of solubility under hydrothermal conditions (Figure 3). The viscosity of nitric acid and sulfuric acid is greater than that of HCl. Hence addition of HCl to NHO_3 would form a more efficient solvent for the growth of RVO_4. The dissolution for rare earth vanadates in HCl and HNO_3 is a process of complex formation between R^{3+}, V^{5+} and the ligands present in the solution OH^-, H_2O, Cl^-, NO_3^-. With a rise in temperature, the association of Cl^- with H^+ increases the yield of HCl and destabilizes the R^{3+} complex. Under these circumstances, nitrates replace chloride ligands. Finally, the nucleation takes place by the polymerization of tetrahedral R^{3+} complexes. Figure 4 shows the solubility of RVO_4 with different solvents.

Gd^{3+} ion is closer in size to Nd^{3+} than Y^{3+} [22]. Hence larger concentrations of Nd impurity ions be grown into the Gd-based crystals than into the Y-based crystals, leading to an increase in the absorption coefficient [23], since, this leads to an increased pumping efficiency, Gd based crystals are good candidates for future use in miniaturized Nd Lasers [24].

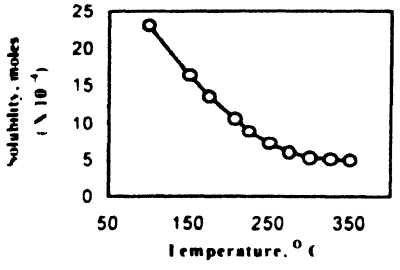

Figure 3. Solubility curve of Nd : YVO_4

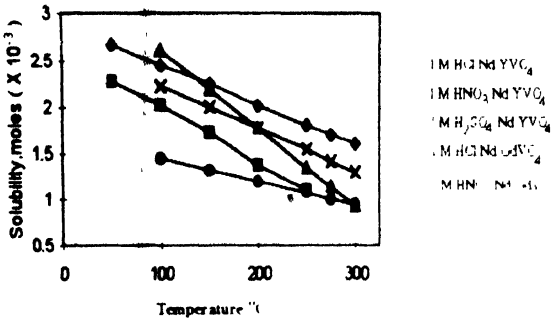

Figure 4. Solubility of RVO_4 in different solvents

Thus, the problems encountered in the growth of rare earth vanadates by melt and the flux techniques have been overcome by hydrothermal technique. The growth and morphology of the crystals strongly depend on the pH of the media and pressure.

3.2. Hydrothermal growth of alkali rare earth tungstates :

Alkali rare earth tungstates form an important group of technological materials due to their excellent luminescence properties and good electrical conductivity. There are many reports on the hydrothermal synthesis of alkali rare earth tungstates [25,26], but the PT conditions of synthesis were quite high (T = 700–900°C, P = 2–3 Kb), and the method appeared quite complicated.

In the present work, the starting materials such as WO_3, $La(NO_3)_3$, NaOH were taken in the following molar ratio : Na_2O : La_2O_3 : WO_3 = 12–18 : 1 : 18–23 and placed inside the teflon liner. Several mineralizers such as HCl, HCOOH, H_2SO_4, HNO_3, and mixed mineralizers like HCl + HCOOH, HCl + H_2SO_4, and HCOOH + HNO_3 with varying concentrations have been tried. Only NaOH was proved to be the most suitable mineralizer for the growth of alkali rare earth tungstates. The crystallization was carried out in all the experiments through spontaneous nucleation. The pH of the medium was varied from 7–11, and good quality single crystals were obtained in the pH range 8.4–8.8. The crystals obtained by the earlier workers under higher PT conditions were smaller and more equi-dimensional. The probable reason for the small crystals may be the higher ionic mobility, low viscosity, and higher concentration of solute ions. The crystals obtained in the present work are well developed, bigger in size, and of good quality. Also, the present experimental conditions are ideal because, more controlled diffusion of ions exists at a relatively lower temperature due to high viscosity, high density, and high dielectric constant and less thermal strain which leads to well-developed crystals.

The formation of $NaLa(WO_4)_2$ takes place under hydrothermal conditions according to the following reactions :

$$2NaOH(aq) + WO_3(s) \rightarrow Na_2WO_4(aq) + H_2O(aq)$$

$$La(NO_3)_3 + 3NaOH \rightarrow La(OH)_3(s) + 3NaNO_3(aq)$$

$$2La(OH)_3 + 3WO_3(s) \rightarrow La_2(WO_4)_3 + 3H_2O$$

$$La_2(WO_4)_3 + Na_2WO_4(aq) \rightarrow 2NaLa(WO_4)_2$$

$$4NaOH(aq) + 2WO_3(s) + La(NO_3)_3(s) \rightarrow NaLa(WO_4)_2 + 3NaNO_3 + 2H_2O$$

The tungstate ions polymerize in acid solution to give meta- and paratungstate ions The degree of polymerization in solution increases as the pH is lowered. Lanthanide ions, in spite of high charge (+3), have low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number. Since ionic size decreases from La^{3+} to Lu^{3+}, the basicity of hydroxides decreases in the same order. Thus $La(OH)_3$ is the strongest and $Lu(OH)_3$ is the weakest base. $La(OH)_3$ precipitates during the reaction as follows :

$$La(OH)_3 + n - 3 \rightarrow La(OH)_n^{(n-3)-}$$

And later dissolves in NaOH solution through any one of the earlier quoted reactions Like La complexes, we can also expect Na La complexes such as $Na_8La(OH)_{3+1}$ in the solution [27]. Being a good base, $La(OH)_3$ reacts with WO_3 to form lanthanum tungstates, which in turn dissolves in normal sodium tungstate to form $NaLa(WO_4)_2$ crystals under controlled conditions. The use of NaOH in the system and the formation of $La(OH)_3$ in the course of the reaction are quite useful in the complexation process. The heavier lanthanide under the same experimental conditions does not give the crystals. The reason for this may be due to the decrease in the basicity with an increase in the atomic number Hence, the synthesis of $NaLn(WO_4)_2$ (where Ln = Pr – Lu) insists on the use of other solvents.

The Figure 5 shows the variation in the growth rate and morphology of $NaLa(WO_4)_2$ crystals with the pH of the growth medium.

3.3. Crystal growth of superionic phosphates :

$HNaMP_2O_7$ (where M = Mn, Co, Ni, Zn, Cd, Pb) crystals are found to be the potential superionic conductors. The experiments were carried out in Morey autoclaves provided with teflon liners within the temperature range 200–250°C, and in the pressure range 80–100 bars. The starting materials such as oxides/nitrates of Mn, Co, Ni, Zn, Cd, Pb were added to the reaction vessel along with the calculated amount of 85% H_3PO_4 and the alkaline component. By this procedure the following superionic pyrophosphates have been obtained : $HNaMP_2O_7$ (where M = Ni, Co, Mn, Zn, Cd), $Na_2H_3Al(P_2O_7)_2$, $(Na_{2/3}Zr_{1/3})_2P_2O_7$, and $NaMP_2O_7$ (where M = Ni, Co, Mn, Fe). The crystallization was carried out by spontaneous nucleation [28]. Solvents like NaOH, HNO_3, HCl, H_2SO_4,

HCOOH, *etc.*, have been used. The hard bases H_2O, OH^-, PO_4^{3-}, NO_3, and SO_4^{2-} act upon the dissolution of the solute and solvated complexes determining the solubility of the final

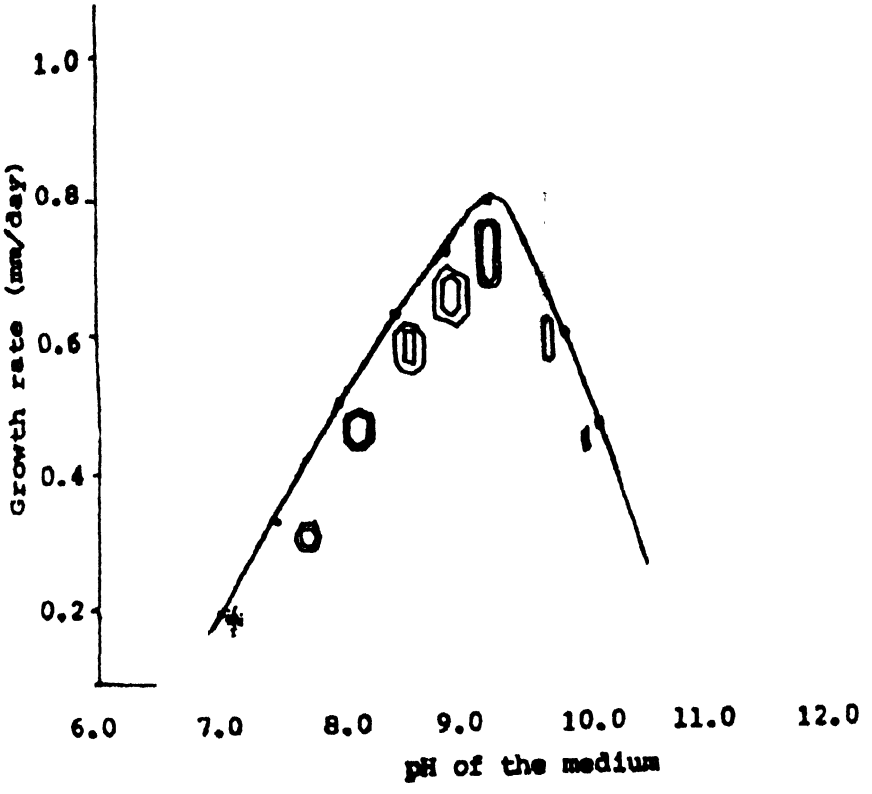

Figure 5. Morphology variation with pH of the media of $NaLa(WO_4)_2$ crystals

resultant stable complex [12]. The following reaction series can be proposed for the formation of $HNaCoP_2O_7$:

$$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O \quad (13)$$

$$3Co(NO_3)_2 + 2H_3PO_4 \rightarrow Co_3(PO_4)_2 + 3H_2O + 6NO_2\uparrow + 3[O]\uparrow \quad (14)$$

$$Zr(NO_3)_4 + 4NaOH \rightarrow 4NaNO_3 + 2H_2O + ZrO_2\downarrow \quad (15)$$

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O \quad (16)$$

$$Na_3PO_4 + H_4P_2O_7 \rightarrow NaH_3P_2O_7 + HNO_3 \quad (17)$$

$$Na_3PO_4 + H_4P_2O_7 \rightarrow NaH_3P_2O_7 + Na_2HPO_4 \quad (18)$$

$$Co_3(PO_4)_2 + H_4P_2O_7 + 4H_2 \rightarrow H_2CoP_2O_7 + 2H_3PO_4 + 2Co(OH)_2 \quad (19)$$

$$Co(NO_3)_2 + H_4P_2O_7 \rightarrow H_2CoP_2O_7 + 2HNO_3 \quad (20)$$

$$NaOH + H_2CoP_2O_7 \rightarrow HNaCoP_2O_7 + H_2O \quad (21)$$

$$Co(OH)_2 + NaH_3P_2O_7 \rightarrow HNaCoP_2O_7 + 2H_2O \quad (22)$$

The formation of a stable complex, *i.e.*, $HNaCoP_2O_7$ at 250°C and 100 bars pressure, must have undergone several intermediate stages of solvation, forming stable and unstable solvated complexes like $NaNO_3$, having very low values of lattice energy constant, 755 KJ/mole, and Co, which has a desolvation energy value around 15 eV, *etc.* have further interacted with each other because of their weak ionic bonding of very low charge to give a stable coordinated compound having a very high lattice energy constant and stronger ionic bonding. But at temperatures around 250°C, the polymerization of the ortho-group of phosphates to form the pyro-group with higher lattice energy may be expected. Also, the reaction between the alkali pyrophosphate complexes with metal complexes results in the formation of stable complexes of pyrophosphate, *i.e.*, $HNaCoP_2O_7$.

The hydrothermal crystallization of these superionic phosphates has been studied through another approach, which is quite effective from the point of hydrothermal solution chemistry.

The crystallization process involves many chemical interactions leading to the formation of a stable complex. To understand the growth of title compounds, the authors have described the following possible stages of interactions :

(i) acid-base interactions,

(ii) formation of metal-aqua complexes, and

(iii) interaction between acid-base and metal-aqua complexes.

(i) Acid-base interactions :

Components such as H_2O, OH^- and PO_4^{3-} are considered as the hard bases and form pyrophosphate complexes at around 250°C [29] :

$$2H_3PO_4 \rightarrow H_4P_2O_7 + 2H_2O \quad (16a)$$

$$NaOH + H_4P_2O_7 \rightarrow NaH_3P_2O_7 + H_2O \quad (23)$$

As the pH increases the stability of $NaH_3P_2O_7$ decreases (pH > 3), and this leads to the formation of $Na_2H_2P_2O_7$

$$NaOH + NaH_3P_2O_7 \rightarrow Na_2H_2P_2O_7 + H_2O \quad (24)$$

The occurrence of eq. (24) also increases the pH of the system, but the compound $Na_2H_2P_2O_7$ is stable in the pH range 3–9. The formation of $Na_3HP_2O_7$ is favoured if pH > 9

$$NaOH + Na_2H_2P_2O_7 \rightarrow Na_3HP_2O_7 + H_2O \quad (25)$$

(ii) Formation of metal-aqua complexes :

The zinc metal-aqua complexes in the hydrothermal system have been studied in detail. The tendency of zinc towards a tetrahedral coordination is evidently responsible for the existence of $\left[Zn(H_2O)_x(OH)_{4-x}\right]^{x-2}$ type aqua complexes in aqueous solutions, where the value of x depends on the pH of the medium [30]. In strongly alkaline solutions, $Zn(OH)_4^{2-}$ occurs (and here $x = 0$). On reducing the solution pH to neutral, a dizincate $\left[Zn_2O(H_2O)_x(OH)_{6-x}\right]^{x-4}$ may be formed as a result of the association of zincate ion.

The zinc oxide forms aqua complexes when dissolved in alkaline solutions [14]. The distribution of zinc aqua ions in alkaline solution is shown in Figure 6 [31].

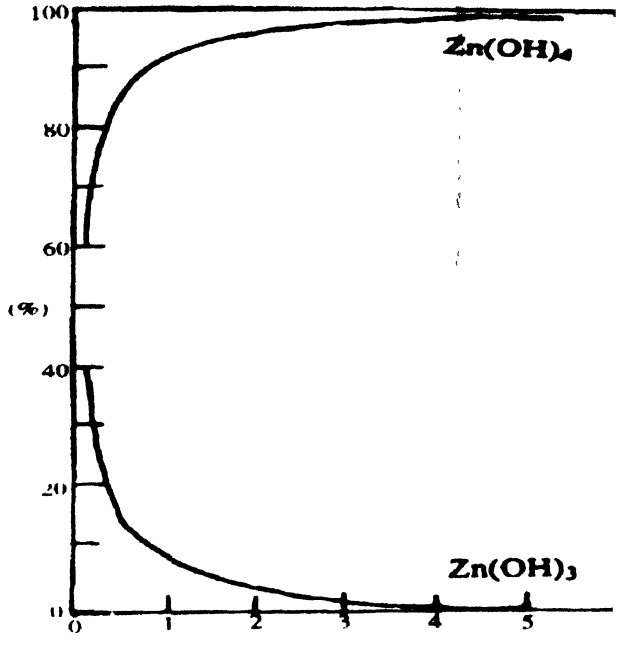

Figure 6. Distribution of zinc aqua ions with respect to the concentration of alkali solutions

Similar aqua complexes can be expected for the other divalent cations, like Mn^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+} and others, under hydrothermal conditions.

Although the metal cations form octahedral complexes, tetrahedral complexes are the more stable of the types of complexes, and a few octahedral complexes retain their constitution for a long time depending upon their half-life of aqua ligands [32].

(iii) Interactions between acid-base and metal-aqua complexes :

Pyrophosphoric acid forms salts due to the sequestering action of the pyrophosphate radical, the sequestering ability decreases with higher concentrations of salts, or with increasing pH. Interactions between metal-aqua complexes with the sodium salts of pyrophosphoric acid can be written as follows :

$$NaH_3P_2O_7 + M(OH)_2 \rightarrow HNaMP_2O_7 + 2H_2O \quad (26)$$
$$(pH = 2\text{–}3)$$

$$Na_2H_2P_2O_7 + M(OH)_2 \rightarrow HNaMP_2O_7 + NaOH + H_2O \quad (27)$$
$$(pH = 3\text{–}9)$$

$$Na_3HP_2O_7 + M(OH)_2 \rightarrow HNaMP_2O_7 + 2NaOH \quad (28)$$
$$(pH > 9)$$

where M = Mn, Fe, Co, Ni, Cu, Zn, Pb.

The aqua complexes can form more stable complexes because of the higher desolvation energy of metal cations when compared to sodium (3.97 eV). Hence, formation of $HNaMP_2O_7$ is expected in the system instead of stable sodium salts of pyrophosphoric acid, namely $Na_2H_2P_2O_7$ and $Na_4P_2O_7$.

The hydrothermal growth of $HNaMP_2O_7$ (where M = Mn, Co, Ni, Zn, Cd, Pb) crystals clearly show that there is a gradual change in the crystallinity and morphology from Mn end to the Pb end. The Table 1 shows the cations in superionic pyrophosphates As evident from the Table 1, higher the entropy values, lower will be the degree of crystallinity and the crystal morphology. For example, $HNaMP_2O_7$ (M = Mn, Co, Al, Ni)

Table 1. Cations in superionic pyrophosphates

Element	At No.	At. Wt	At radi* (Å)	Entropy at 298°K (e.u)
Al	13	65.38	1.82	6 769
Mn	25	54.93	1 79	7.590
Co	27	58 93	1.67	6 800
Ni	28	58 70	1 62	7.137
Zn	30	65.38	1.53	9.950
Cd	48	112.41	1.71	12 300
Pb	82	207.20	1 81	15.490

*ref. Table of periodic properties of the elements (Sargent-Welch Scientific Company)

show good crystallinity and well developed crystal morphology, whereas the crystals $HNaMP_2O_7$ (M = Zn, Cd, Pb) with higher entropy values have lower degree of crystallinity and crystals show poor morphology and often polycrystalline [33].

4. Conclusions

The above studies contribute to the understanding of the hydrothermal crystallization process. Also help in selecting the suitable solvents, their concentration, and role in the crystallization process including the PT conditions of crystallization of even high temperature structural materials like titanates, phosphates, silicates, tungstates, and so on. The reduction in the PT conditions makes this technique more popular not only for crystal growers, but also for other specialists dealing with the aspects of materials processing, Thus making the hydrothermal technique more versatile and highly adaptable for hydrothermal sintering, hydrothermal epitaxy, hydrothermal electrochemical, and so on. Further reduction in PT conditions would help in the use of glass/silica autoclaves, which would facilitate the *in-situ* observation of the hydrothermal crystallization process. Since, the energy requirement is minimized, the chemicals can be less hazardous in case of accidents, more environmentally friendly—the technique can be clubbed under the soft, solution processing.

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